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The role of alloying element on the behaviors of helium in vanadium: Ti as an example

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ABSTRACT

Using a first-principles method, we present the effect of the alloying element Ti on the behaviors of He in vanadium. Away from Ti atom, He migrates from one tetrahedral site to another with a barrier of 0.06 eV. When He moves towards the Ti, its energy barrier increases to ~0.19 eV. With the presence of Ti in vacancy vicinity, the binding energies of He to He_{n-1}-vacancy cluster decrease compared with that in pure vanadium, indicating that the alloying element Ti can diminish the binding of He with vacancy in vanadium. This confirms that the He retention in vanadium can be suppressed by doping Ti in experiments. All the interactions between a tetrahedral He and He_{n-1}-$vacancy_m$ (n/m = 1, 2, 3, 4) cluster are attractive in the vicinity of Ti. For a given value of m/n, the He binding energies to the cluster decreases/increases with the increasing number of He/vacancies.

1. Introduction

The interaction between helium (He) and metal or metal-alloy has great scientific interest in condensed matter [1–4]. For instance, the realization of nuclear fusion energy rests with the development of key materials in the thermonuclear fusion device Tokamak, in which the choices of the first wall [5–11] and structural material [2–4] are considered as two key issues. In the nuclear fusion reactor, the structure material irradiated by the 14.1 MeV high energy neutron experiences a variety of transmutations and radiation damages. Then, the produced He via the (n, α) transmutation reaction can be easily trapped by the defects such as vacancies or void [12], which has been attested in real materials in many experiments [13–15]. In turn, the accumulation of He can cause the bubble formation and void swelling [16,17], and further result in the embrittlement of the structural material.

Vanadium-alloys have been attested to be the promising candidate of the structural material in fusion reactor owing to the excellent performance at the high temperature [18–20] and intrinsic low activation property [21–24], which meets the requirement for safety operation in the extreme conditions. Previously, there were many studies on the retention, diffusion, and permeation properties of the impurities such as H, C, N, O in pure vanadium and vanadium-based alloys both experimentally [25–30] and theoretically [31–34]. According to these research results, it is important to note that the alloying element can obviously affect the mechanical properties of vanadium, as well as the electronic properties of impurities in vanadium. For instance, Lee et al. gave the effect of alloying element (Fe, Ni, Al, Ti, and Nb) on H electronic structure in vanadium [35], which indicates that these alloying elements have a large effect on the solution behaviors of H. The effective volume of the alloying element follows the sequence Nb > Ti > Al > Ni > Fe. The H solution energy can averagely be decreased in the alloying element vicinity by the larger volume. Also, the doping of Ti in vanadium not only decreases the content of O in the deterioration of vanadium but also substantially inhibit the swelling of material [36–38]. Concerning the topic of current study, the behaviors of He in vanadium and vanadium-alloys have been also reported recently in theoretical [39–43] and experimental studies [44]. Seletskaia et al. systematically investigated H defect properties in bcc transition metals such as vanadium, molybdenum, niobium, tantalum, and tungsten [39]. They found that a single He atom prefers to occupy the tetrahedral interstitial site in prefect

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host metals, while the most stable site is vacancy in comparison with interstitial sites. Also, they demonstrate that the He formation energy is strongly dependent on the electronic structure of the host. Using first-principles method, Zhang et al. [41] investigated the energetics, stability, and migrating behavior of He, vacancies, and He-vacancy clusters in vanadium. Further, Li et al. [40] again studied the microscopic mechanism for He capturing in two kinds of vacancy defects including monovacancy and 9-atom void. In a monovacancy, the behaviors of He are consistent with the results obtained by Zhang et al. [41], while a 9-atom void can capture as many as 66 He atoms with internal pressure of 19.3 GPa. At the same time, Zhang et al. [42] also investigated the behaviors of He in Cr–Ti–vanadium ternary alloy and found that the tetrahedral site is still the most stable configuration for interstitial He atom. Recently, Zhang et al. [43], with first-principles calculations, again presented the stability and energetics of H–He-vacancy to find out the synergistic interplay among these defects in pure vanadium.

Up to now, it is still unknown how the alloying elements interact purely with He atom in vanadium, although there are some experimental researches on the behaviors of He implanted into Ti–vanadium alloy. For instance, Liu et al. [44] studied the behaviors of He implanted into a vanadium–4Ti alloy using a 5 keV He ion beam and analyzed the retention of He by a technique of thermal desorption spectroscopy (TDS). We know that He is considered as a kind of harmful impurity in structural material vanadium so that it can easily destroy the intrinsic properties of vanadium. To suppress the damaged effect of He, in this paper, we try to add alloying elements Ti that will be found to be one of good alloying elements to suppress the binding of He at vanadium. By using the first-principles method based on the density functional theory, we investigate the effect of Ti on the structure, diffusion, and vacancy capturing behaviors of He atom in vanadium. In other words, we investigate the structure, diffusion, and vacancy capturing behaviors of He atom in a dilute Ti–vanadium alloy. We expect that these results could provide a useful reference for further understanding the microscopic mechanism of He bubbles and He embrittlement in vanadium and vanadium-alloys.

2. Computational method

The first-principles calculations were performed using the Vienna Ab-initio Simulation Package (VASP) code [45,46] based on the density function theory (DFT). We adopted the generalized gradient approximation (GGA) with the Perdew and Wang (PW91) functional [47] for the exchange-correlation interaction and the projector-augmented wave (PAW) potentials [48] for the ion-electron interaction. The plane wave energy cutoff is 350 eV, which is sufficient for the total energy and geometry of supercells. During the geometry optimization for Ti–vanadium supercell, the Brillouin zone was sampled in terms of the Monkhorst-Pack scheme [49] and the Methfessel-Paxton smearing with a width of 0.20 eV. The calculated equilibrium lattice constant for bcc vanadium is 2.98 Å, in good agreement with the corresponding experimental value of 3.03 Å [50], which demonstrated the accuracy of the current PAW method. For the calculations of the formation and binding energies of defects, a bcc supercell of 128-atom with 127 vanadium atoms and one Ti atom was used. Here we need to point that the concentration (i.e., composition) of Ti is 0.78% in metal vanadium, which corresponds to a dilute Ti–vanadium binary alloy, i.e., $Ti_{0.78}vanadium_{99.22}$ alloy. The Brillouin zones were sampled with $3 \times 3 \times 3$ k-points by the Monkhorst-Pack scheme [49]. During calculations, the supercell size, shape, and atomic positions were relaxed to equilibrium, and structural optimization were performed until energy change on each atom is less than 10^{-5} eV and forces on each atom less than 0.001 eV/Å. According to the two setting values, we have performed the convergence tests on all the relevant energies. The results demonstrate that the total, formation, and binding energies are converged to within less than 1 meV/atom. Also, the two setting values are shown to ensure that interaction energy difference of defects (e.g. vacancy and impurity He) between supercell repetitions were converged to within less than 1 meV/atom.

To determine minimum energy migration path for the interstitial He migration in pure vanadium and Ti–vanadium alloy, we employ the climbing image nudged elastic band (NEB) method [51]. Atomic positions are linearly interpolated to set up images along the migrating path connecting the initial and final positions, and allowing the migrating atom as well as all the other atoms of the supercell to fully relax. The energy difference between the minimum and transition state is migration energy barrier.

3. Results and discussion

3.1. Energetic stability of He in vanadium and Ti–vanadium alloy

First, we investigate the thermodynamic stability of single He atom in pure vanadium. It is well known that impurity He atoms are insoluble in many metals and prefer to occupy the interstitial sites when they are produced by transmutation reaction via high energy neutron irradiation or by implantation method experimentally [52–54]. For simplicity, here we only take into account two high symmetry interstitial sites, the tetrahedral interstitial site (t-site) and the octahedral interstitial site (o-site). In pure vanadium, the formation energy of interstitial He atom can be given as:

$$E_{He}^{f} = E_{vanadium,He} - E_{vanadium} - E_{He}, \quad (1)$$

where $E_{vanadium,He}$ is the energy of the vanadium supercell with one interstitial He atom, $E_{vanadium}$ is the energy of the perfect vanadium supercell, and E_{He} is the energy of an isolated He atom in a large vacuum supercell. The calculated results indicate that a single He prefers to stay at the t-site with a formation energy of 2.98 eV, which is 0.19 eV lower than that at the o-site, as shown in Table 1. Our calculated values are consistent with previous results by Zhang et al. [31] and Gui et al. [54], respectively.

Next, we turn to study the stability of He atom in the presence of alloying element Ti and compare it with pure vanadium case. In our previous work [55], the formation energies of both interstitial and substitution Ti in vanadium have been examined. A single Ti atom prefers to occupy the substitution site (s-site) since the s-site can open up more space to accommodate a Ti atom. Here, we also put a single He atom at the t-site and o-site, respectively, and both t-site and o-site are the first nearest neighbor (1NN) sites of substitution Ti atom in vanadium, as shown in Fig. 1. The formation energy of the interstitial He atom in the dilute Ti–vanadium binary alloy can be given as:

Table 1
The formation energies (eV) of one He atom in pure vanadium and Ti–vanadium alloy with or without ZPE.

Metal	ZPE of He (eV)		Formation energy of He (eV)	
	T-site	O-site	T-site	O-site
Vanadium	0.091 0.089[a]	0.079 0.049[a]	2.98, 3.07[ZPE] 3.02, 3.11[ZPE, a] 2.95[b]	3.17, 3.25[ZPE] 3.24, 3.29[ZPE, a]
Ti–vanadium alloy	0.092	0.080	2.84, 2.93[ZPE]	3.07, 3.15[ZPE]

[a] Ref. [54].
[b] Ref. [31].

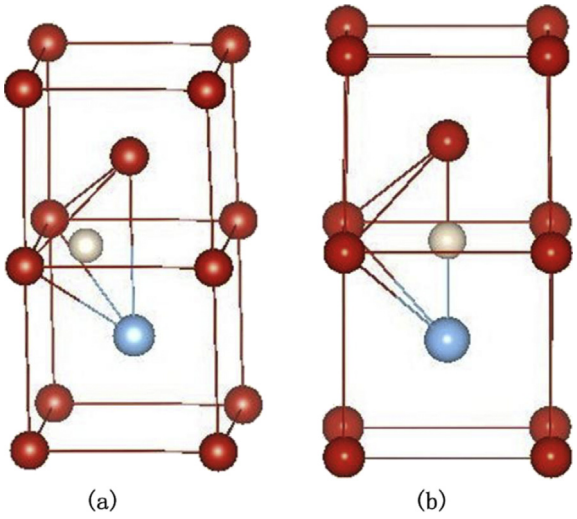

Fig. 1. The interstitial structures of He atom in dilute Ti–vanadium binary alloy: (a) t-site (b) o-site. Small (white), mediate (red), and large (blue) balls represent He, vanadium, and Ti atoms, respectively.

$$E^f_{He} = E_{Ti-vanadium,He} - E_{Ti-vanadium} - E_{He}, \quad (2)$$

where $E_{Ti-vanadium,He}$ represents the energy of the Ti–vanadium alloy supercell with one He atom. $E_{Ti-vanadium}$ is the energy of the perfect Ti–vanadium alloy supercell. After relaxation, the He formation energies are calculated to be 2.84 eV at the t-site and 3.07 eV at the o-sites, respectively. Table 1 shows the formation energies (eV) of He atom in pure vanadium and Ti–vanadium alloy. From Table 1, we can see that a single He atom is also favorable to occupy the t-site in Ti–vanadium alloy. But, there is a little difference on the formation energy of He atoms, and the energy difference is 0.14 eV in the t-site (0.10 eV in the o-site) between in pure vanadium and in Ti–vanadium alloy. This reflects that the alloying element Ti can slightly affect the formation energy of He at the interstitial sites in vanadium.

As to the binding properties between Ti and 1NN interstitial He in vanadium, we observe a weak Ti–He interaction in the both t-site and o-site. If we choose an isolated Ti atom and an isolated He atom as references, the binding energies between either t-site He atom or o-site He atom and Ti in a vanadium matrix are shown to be negative, meaning that Ti–He interaction in the t-site or o-site are repulsive in vanadium.

Generally, the zero-point energy (ZPE) is taken into account to study the electronic structure and stability of H in metals owing to that H is the lightest element in nature. Helium is lighter element in nature so that its ZPE also needs to be considered when studying its thermodynamic behavior in metals and metal-alloys so that we can get accurate absolute values of He atom formation energy. The reason is that the $h\nu$ is generally larger than kT (~0.026 eV) at low or room temperature, here ν represents a real normal mode frequency. In this study we find that when He atom occupies the T-site, $h\nu$ are 0.091 eV and 0.092 eV in pure vanadium and Ti–vanadium alloy, respectively. The two results are notably larger than 0.026 eV. In the current calculation, the ZPE can be obtained by $ZPE = \frac{\sum_i h\nu_i}{2}$. The calculated results showed that in pure vanadium, the ZPEs of He atom are 0.091 eV at the t-site and 0.079 eV at the O-site, respectively. We can see that the ZPE of He atom has a significant influence on the absolute values of He atom formation energy in both pure vanadium and Ti–vanadium alloy. The two values are notably larger than the error (0.02 eV) of first-principles calculation. But, the relative stability of He atom in the interstitial sites in both cases remains essentially unchanged, as listed in Table 1. In terms of the current conclusion, we need to point out that the ZPE of He atom should be considered in future investigations if one takes into account the absolute values of the He formation energy in metals and metal-alloys. On the contrary, we do not need to consider the ZPE of He if we only want to know the relative stability of He atom in the solution sites in metals and metal-alloys.

3.2. He diffusion behaviors in pure vanadium and Ti–vanadium alloy

It is well known that bubble formation and growth is related to He atom diffusion in metals and metal-alloys. The main processes involve the interstitial He atom migration and vacancy migration. Of cause, there is other diffusion such as He atom-vacancy cluster by thermal activation or athermal process [56]. Here, we only take into account the interstitial He diffusion to investigate the effect of alloying element Ti on He migration in vanadium.

As mentioned above, He atoms initially occupy the t-sites when they are produced by transmutation reaction via high energy neutron irradiation or by implantation. In pure vanadium, He atom is found to diffuse easily from a t-site to a neighboring one, with a barrier of 0.06 eV, consistent with the result calculated by Zhang et al. [31]. With the presence of the alloying element Ti, we further analyze the diffusion energy landscape of He migration between two different t-sites, as plotted in Fig. 2. One notes that some particularly high energy barriers are present due to the doping of Ti in vanadium. We believe that there are two possible reasons resulting in such a phenomenon: one through the short-range repulsion between the tetrahedral He atom and Ti and the other through a local stress field. The atomic radius of Ti (1.46 Å) is larger that of vanadium (1.35 Å). The embedding of Ti will thus lead to the local stress field in the vicinity of substitution Ti, which forces the energy barrier increase of interstitial He atom. The energy barrier of an interstitial He atom migrating from a 2NN site of Ti to a 1NN (c → b path) is 0.13 eV, about twice as much as one in pure vanadium case 0.06 eV, while the energy barrier from a 3NN to a 2NN site of Ti is about 0.11 eV (d → c path), further it is to see that the energy barrier (0.06 eV) is almost the same as in pure vanadium exceeding 3NN site (e → d path). For a tetrahedral He atom to migrate from a 1NN to another 1NN of Ti, i.e., b → a path, the energy barrier is found to be 0.018 eV. Vice versa, He atom moves away from the Ti atom along the opposite diffusion path, the energy barriers are 0.052 eV (b → c path) and 0.034 eV (c → d path). This is similar to the behaviors of He atom in pure vanadium.

3.3. Effect of alloying element Ti on He clusters in vanadium

The formation of He clusters plays a key role in He bubble

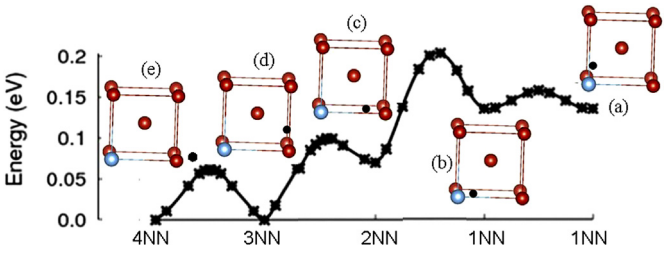

Fig. 2. Diffusion energy landscape for the tetrahedral He migration path in the vicinity of a Ti atom. The most stable and metastable structures are also plotted. Small (black), mediate (red), and large (blue) balls represent He, vanadium, and Ti atoms, respectively.

growth in metals and metal-alloys. To study the behaviors of He_n clusters inside the supercell of Ti–vanadium binary alloy, we put two, three, and four He atoms into the neighboring t-sites, respectively. The positions of He and metal atoms are allowed to relax, which can make He atoms search their energetically favorable sites.

First, we have calculated the formation energies for He_n (n = 2, 3, 4) clusters around Ti atom in vanadium, as listed in Table 2. It is clear to see that, in the vicinity of Ti atom, the formation energies of He_2, He_3, and He_4 clusters in vanadium are 5.16 eV, 8.06 eV, and 10.77 eV, respectively. The values are very high and demonstrate that the He gathering into a bubble is not favorable. Moreover, the formation energy increases with the increase of He atom number. Thus, from the viewpoint of formation energy, we cannot see the attraction or repulsion among the multi-He atoms around Ti atom.

Next, we investigate the binding properties of He_n clusters. The binding energy among He_n is defined as

$$E^b_{nHe} = nE_{Ti-vanadium,He} - \left[E_{Ti-vanadium,nHe} + (n-1)E_{Ti-vanadium}\right], \quad (3)$$

In the above equation, $E_{Ti-vanadium,He}$ is the energy of the Ti–vanadium supercell containing a tetrahedral He only and $E_{Ti-vanadium,nHe}$ is the energy of the Ti–vanadium supercell containing n tetrahedral He. All the supercells contain the same number of metal sites, i.e. have the same size. A positive/negative binding energy means attraction/repulsion among n He atoms.

Concerning the He_n cluster, their binding energy correspond to $He_{t\text{-}site} + He_{n-1} \rightarrow He_n$ reaction. The atomic structures and binding energies among n He atoms are shown in Fig. 3 and Table 2, respectively. The binding energy between two He atoms is 0.53 eV. With the adding of the third He atom, we observe that the binding energy of a $He_{t\text{-}site}$ to He_2 cluster is 0.46 eV and decreases slightly in comparison with He_2 cluster case, meaning that the binding of the third $He_{t\text{-}site}$ to He_2 cluster is not stronger than two He atoms (i.e., He_2 cluster). However, with the adding of the fourth He, the binding energy of a $He_{t\text{-}site}$ to He_3 cluster again increases to 0.59 eV, and thus the binding of the third $He_{t\text{-}site}$ to He_3 cluster becomes more energetically favorable than the both He_2 and He_3 clusters. Although there is the variation trend for the energy, we demonstrate that the binding energies for these clusters are found to be positive in all cases from He_2 to He_4 clusters, suggesting that these interactions are attractive. Such self-trapping of He atoms in Ti–vanadium alloy as well as other metals [52,53] should be originated from the fast and easy diffusion property of interstitial He as investigated above. At the same time, the behavior of self-trapping of He atoms could be expected to be responsible for the He bubbles formation observed macroscopically at low temperatures in metals, such as Au [57]. For comparison, we have also calculated the binding energies of He_n clusters from He_2 to He_4. Table 2 lists the detailed values, together with the previous results obtained by Zhang et al. [41]. The binding energy between two He atoms in vanadium is only 0.02 eV, consistent with the previous result using the same simulation method [41]. We observe that the binding energy of He_2 in vanadium is obviously lower than that in Ti–vanadium alloy, but the interaction between two He atoms is still attractive. For He_n cluster with n = 3, in the present calculation the binding energy is 0.26 eV, close to 0.21 eV obtained by Zhang et al. [41]. But, The two values are lower than that in Ti–vanadium system. With the fourth He atom adding into the He_3 cluster to form He_4 cluster, the binding energy in vanadium is 0.54 eV, close to 0.59 eV of the He_4 cluster in Ti–vanadium alloy. As shown in Table 2, Zhang et al. gave the binding energy of 0.06 eV for He_4 cluster in vanadium. This value is notably smaller than 0.54 eV we obtained, a relatively larger difference of 0.48 eV is present between us. The possible reason might be originated from the difference of "atomic relaxing mode". During the calculations, we note that Zhang et al. relax all the atomic positions at a constant supercell volume, which is different from the current computational method. Therefore, the "atomic relaxing style" will have a large influence on the binding energy for the bigger He_n cluster in the calculations because the larger local stress is generally present around the bigger He_n cluster at a constant supercell volume.

Table 2
The formation and binding energies of He_n clusters (n = 2, 3, 4) in dilute Ti–vanadium binary alloy and pure vanadium (all energies in eV).

Configurations	Ti–vanadium		Vanadium	
	E^s	E^b	E^s	E^b
He_2	5.16	0.53	5.90, 5.88[a]	0.02, 0.02[a]
He_3	8.06	0.46	8.62, 8.67[a]	0.26, 0.21[a]
He_4	10.77	0.59	11.31, 11.69[a]	0.54, 0.06[a]

[a] Ref. [41].

Fig. 2 shows the atomic structures of these He_n clusters. For He_2 cluster, the two He atoms tend to pair up at two neighboring t-sites and the equilibrium distance is 1.92 Å. To a He_3 cluster, the most stable structure is a triangle with the average He–He distance of 1.87 Å, while for the He_4 cluster, the most stable configuration is an irregular tetrahedron with the average He–He distance of 1.89 Å. It can be seen that the average distance between He atoms is close to 1.90 Å among these He_n clusters in alloying element Ti vicinity. Further, the cell deformation is not obvious for He_2 cluster after relaxation (Fig. 3(a)), however, the deformation is notably present in the vicinity of He_3 (Fig. 3(b)) and He_4 (Fig. 3(c)) clusters, respectively. We can obviously observe that in the case of He_4 cluster (Fig. 3(c)) the Ti atom has been almost removed from its original position. Therefore, with the further gathering of He atoms, the He_n cluster vicinity has to emit a Ti (or vanadium)-vacancy Frenkel pair to release the local stress in vanadium lattice. In other words, the Ti or vanadium atom in the vicinity of the He_n cluster should be kicked out to form a vacancy when He atoms accumulate into a certain amount. This behavior is basically agreement with the He_n cluster in α-Fe [58] and Cr–Fe alloy [59].

3.4. Effect of Ti on He capturing in vacancy in vanadium

Below, we explore the effect of Ti on He capturing at vacancy in vanadium owing to that vacancies, as a frequent defect in metals, play a key role in the nucleation and growth of He bubbles [60,61]. Fig. 4 shows the possible cases on the vacancy formation in Ti vicinity, i.e., the 1NN, 2NN, and 3NN sites of Ti. The vacancy formation energy is written as:

$$E^f_{vac} = E_{vac,Ti-vanadium} - 126E_{vanadium} - E_{Ti}, \quad (4)$$

where $E_{vac,Ti-vanadium}$ is the total energy of the Ti–vanadium supercell with one vacancy, $E_{vanadium}$ and E_{Ti} are the energies of a single vanadium atom and a single Ti atom, i.e., the chemical potentials of vanadium and Ti.

The vacancy formation energies are listed in Table 3. According to Table 3, one sees that the formation energy of 1NN vacancy of Ti is 0.59 eV, obviously smaller than those of 2NN case (2.57 eV) and 3NN case (2.24 eV), suggesting that the 1NN vacancy should be easily formed around the Ti atom in vanadium. On the contrary, the 2NN and 3NN vacancies of Ti are not easily formed due to the larger formation energies. The value obtained for the vacancy formation energy in pure vanadium has also been 2.23 eV, close to the results of 2NN and 3NN vacancies of Ti, but much larger than that of 1NN

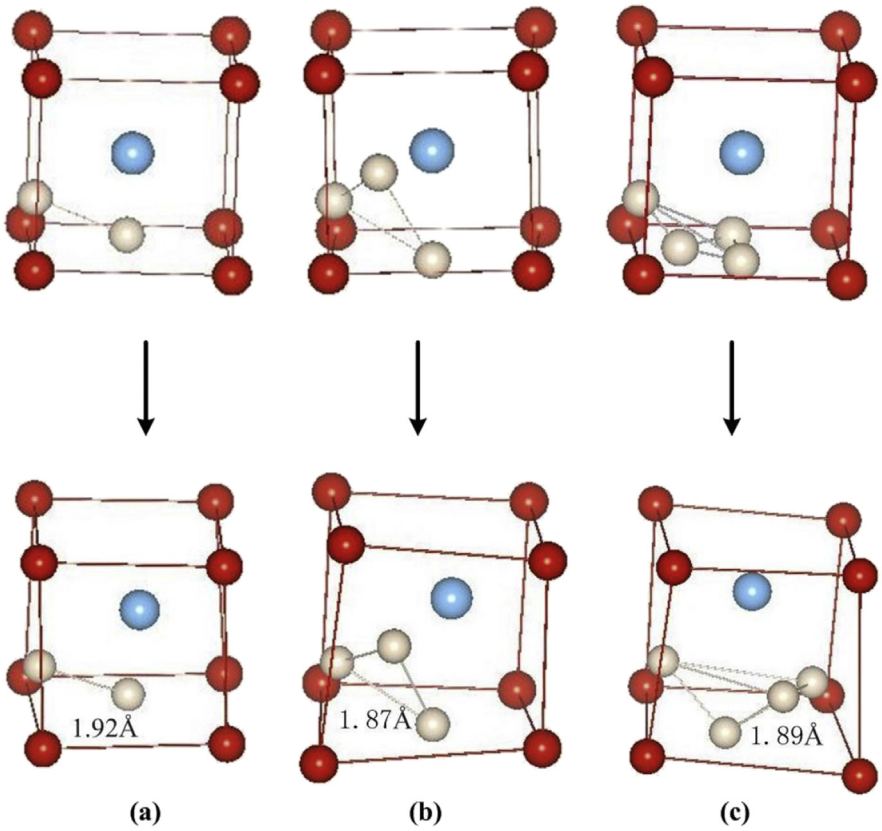

Fig. 3. Schematic diagram of the clusters: (a) He_2, (b) He_3 (c) He_4. Small (black), mediate (red), and large (blue) balls represent He, vanadium, and Ti atoms, respectively.

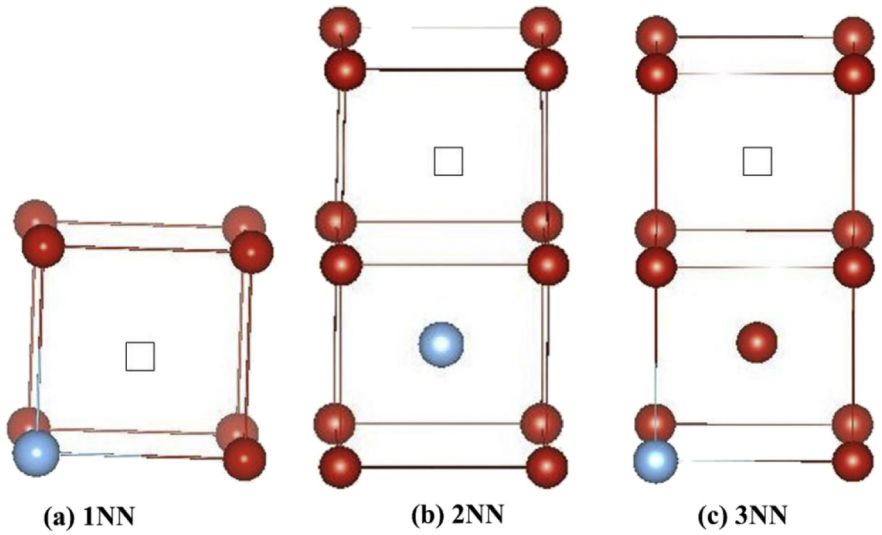

Fig. 4. The three possible vacancies in Ti vicinity (a) 1NN case, (b) 2NN case, (c) 3NN case. Small (red) and large (blue) balls represent vanadium atoms and Ti atoms, respectively. The open square represents vacancy.

Table 3
The vacancy formation energy (eV) in dilute Ti–vanadium binary alloy and pure vanadium (all energies in eV).

Sites	Ti–vanadium alloy			Vanadium
	1NN	2NN	3NN	
E^f_{vac}	0.59	2.57	2.24	2.23

vacancy of Ti. The possible reason could be understood as follow. The presence of Ti can destroy the original vanadium–vanadium interaction. For 1NN vanadium atom of Ti, there exists a Ti–vanadium interaction besides 7 vanadium–vanadium interactions. With regard to 2NN and 3NN vanadium atoms of Ti, there are only 8 vanadium–vanadium interactions, similar to the case of pure vanadium. Thus, owing to that the presence of Ti destroys the intrinsic vanadium–vanadium interaction, taking a vanadium atom to form

a vacancy from 1NN site of Ti should be much easier than that from 2NN or 3NN site of Ti.

After establishing the stability of vacancy in the vicinity of Ti, we now turn to discuss the capturing behaviors of He atoms in a 1NN vacancy in vanadium. The binding energy of He to vacancy is given as

$$E^{b}_{He_n-vac} = \left[E_{Ti-vanadium,He(t-site)} - E_{Ti-vanadium}\right] - \left[E_{Ti-vanadium,He_nvac} - E_{Ti-vanadium,He_{n-1}vac}\right], \quad (5)$$

where $E_{Ti-vanadium,He_nvac}$ and $E_{Ti-vanadium,He_{n-1}vac}$ are the energies of the supercell with one He_n-vacancy and He_{n-1}-vacancy clusters, respectively. $E_{Ti-vanadium,He(t-site)}$ is the energy of the supercell with a tetrahedral He atom, as shown in Fig. 1(a).

Fig. 5 shows the He binding energy captured by a vacancy with the increase of He atoms in pure vanadium and Ti–vanadium alloy. In pure vanadium and Ti–vanadium alloy, the binding energies of the first He atom to a vacancy are, respectively, 0.96 eV and 0.73 eV. The binding energies are positive, indicating that capturing one He atom in an empty vacancy to form a He_1-vacancy cluster is an exothermic process. Such strong binding means that there is an attractive interaction between He atom and vacancy in both metals. Further, multi-He atoms are sequentially put into the vacancy and their structures are also relaxed to the equilibrium states. We observe that the binding energy increases in pure vanadium (1.20 eV) and decreases in Ti–vanadium (0.56 eV) alloy when the second He atom is added into the He_1-vacancy cluster. Thus, the formation of the He_2-vacancy cluster can result in energy releases of 1.20 eV in pure vanadium and 0.56 eV in Ti–vanadium alloy, respectively. With the further increase of He atoms, the energy release continues. It is found that the formation of He_3-vacancy from He_2-vacancy and one tetrahedral He (He_2-vacancy + $He_{t\text{-}site}$ → He_3-vacancy) can result in energy releases of 0.86 eV in pure vanadium and 0.60 eV in Ti–vanadium alloy, and the formation of He_4-vacancy from He_3-vacancy and one tetrahedral He (He_3-vacancy + $He_{t\text{-}site}$ → He_4-vacancy) are also exothermic with energy releases of 0.60 eV in pure vanadium and 0.47 eV in Ti–vanadium alloy, respectively. In the current study, we demonstrate that the binding energies are still favorable when a vacancy captures up to six He atoms. Exceeding six He atoms, we did not give the further investigations. In α-Fe, Xiao et al. has demonstrated that there are at most eight He atoms captured by one vacancy [58], beyond eight He atoms, the vacancy must emit a Frenkel pair to release the substantial stress to further capturing more He atoms. In the current presentation, we note that the lattice distortion and expansion are notably present in the Ti–vanadium lattice with the increase of He number as shown in Fig. 6, although the binding energies of He to He_{n-1}-vacancy cluster are still positive and favorable. For example, as shown in Fig. 6(b) and (c), we can obviously observe that in the cases of He_5-vacancy and He_6-vacancy clusters the Ti and vanadium atoms extend and expand to the surroundings of He_5 and He_6, respectively. So, the Ti or vanadium atom in the vicinity of He_n-vacancy cluster should be kicked out with the accumulation of He atoms to form Frenkel pair and release the substantial stress, which in turn further capture more He atoms. To some extent, such capturing behavior of multi-He by vacancy we have presented in this study is consistent with Xiao's conclusion [58].

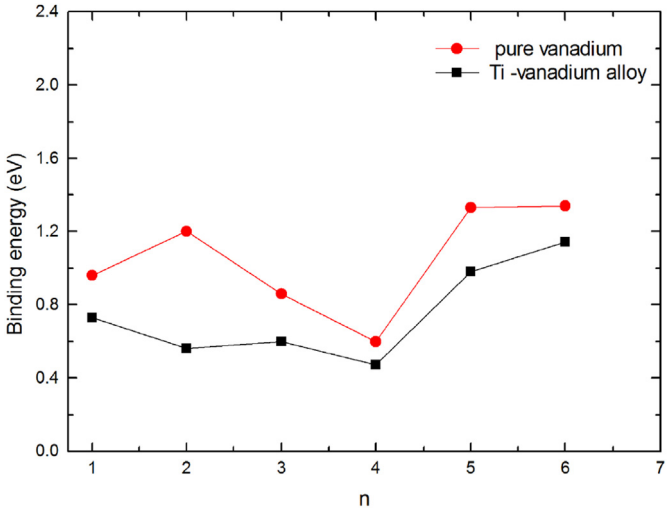

Fig. 5. The binding energy as a function of the number of He atoms at a vacancy in Ti–vanadium and pure vanadium. The energy zero point is the energy of He in the t-site far away from the vacancy.

We now discuss the effect of alloying element Ti on the binding properties between He atoms and vacancy in vanadium. According to the results from Fig. 5, one vacancy can capture up to 6 He atoms in the absence of Ti, similarly, there is the same He trapping number as in pure vanadium with the presence of Ti. Thus, from trapping number of He atoms in vacancy, we cannot see the obvious effect of alloying element Ti. However, with the presence of Ti in the surrounding of vacancy, all the binding energies of He to He_{n-1}-vacancy cluster are found to decrease compared with those in pure vanadium. The decreased value are, respectively, 0.23 eV, 0.64 eV, 0.26 eV, 0.13 eV, 0.35 eV, and 0.20 eV for He_1-vacancy, He_2-vacancy, He_3-vacancy, He_4-vacancy, He_5-vacancy, and He_6-vacancy, and the decreased average value is 0.35 eV. This indicates that the presence of alloying element Ti can diminish the binding of He with vacancy in vanadium. Recently, in fusion reactor, considerable studies has been made to develop vanadium-alloys containing 4% Ti and 4% Cr in experiments [36,62,63]. The research results demonstrate that the doping of Ti in vanadium can substantially suppress the swelling of vanadium. Moreover, Loomis et al. have reviewed the effect of neutron irradiation on tensile strength, ductility, creep, fatigue, ductile-brittle transition temperature, and swelling of Ti–Cr–vanadium alloys [64]. Then, returning to the current first-principles study, our results fully confirm the experiments and can indicate that the retention of He in vanadium can be suppressed by doping the alloying element Ti. As to the interaction between another alloying element Cr and He in vanadium, in the future studies we will give an investigation.

3.5. *Stability of small He_n-$vacancy_m$ clusters*

It is well known that the small He_n-$vacancy_m$ (n/m = 1,2,3,4 …) clusters can be easily formed via further attracting interstitial He atoms in metals or metal-alloys, which can further lead to the larger lattice distortion due to the existence of local stress field in the vicinity of He_n-$vacancy_m$ cluster. When the local stress is beyond the endurance of one $vacancy_m$, the He_n-$vacancy_m$ cluster will has to squeeze out a self-interstitial atom in the vicinity of $vacancy_m$ to release stress and simultaneously form one vacancy, and mutate into a He_n-$vacancy_{m+1}$ cluster. Thus, the resulting in consequence will continuously extrude self-interstitial atom of the host metal to form vacancy. In turn, the forming vacancy can then attract more He atoms to make the bubble grow even bigger, finally causing a cascading effect of He bubble nucleation observed experimentally. For instance, using thermal desorption spectrometry (TDS) method, Kornelsen found that interstitial He atoms were easily captured by He_n-$vacancy_m$ cluster to become more larger He_n-$vacancy_m$ cluster with various size in experiment [65]. In view of this, we also investigate the stabilities of small He_n-$vacancy_m$ cluster around the alloying element Ti in vanadium. The binding

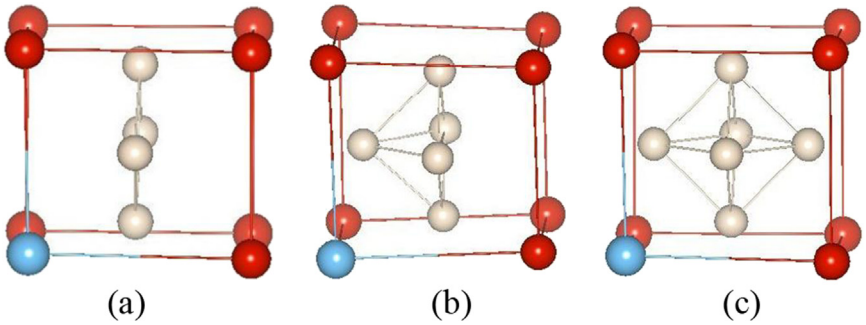

Fig. 6. Atomic structures for 4 He, 5 He, and 6 He at one vacancy in Ti–vanadium alloy. Small (black), mediate (red), and large (blue) balls represent He, vanadium, and Ti atoms, respectively.

energy of a tetrahedral He to the He_{n-1}-$vacancy_m$ cluster is given as

$$E^b_{He_n vac_m} = \left[E_{Ti-vanadium,He(t-site)} - E_{Ti-vanadium}\right] - \left[E_{Ti-vanadium,He_n vac_m} - E_{Ti-vanadium,He_{n-1} vac_m}\right], \quad (6)$$

where $E_{Ti-vanadium,He_n vac_m}$ and $E_{Ti-vanadium,He_{n-1} vac_m}$ are, respectively, the energies of the supercell with one He_n-$vacancy_m$ and He_{n-1}-$vacancy_m$ clusters.

Fig. 7 plots the binding energies of the tetrahedral He to the He_{n-1}-$vacancy_m$ cluster. The binding energies are found to be positive in all cases, indicating that their interactions are attractive in the vicinity of Ti in vanadium. We believe that the easy diffusion interstitial He as well as the self-trapping of He atoms investigated above should play a key role in the formation of He_n-$vacancy_m$ cluster. For a given value of m, the interstitial He binding energies to the cluster totally decreases with the increasing number of He, but for a given value n, the binding energies of He increases as a function of the number of vacancies for each cluster. This fully demonstrates that the increase of cluster pressure stems from the gathering of He atoms, which have been confirmed by previous theoretical studies [52] and experimental results [66,67].

4. Summary

We have carried out first-principles calculations to investigate the effect of the alloying element Ti on the behaviors of He in a dilute Ti–vanadium binary alloy. The main summaries are below.

(i) Similar to that in pure vanadium, a single He atom still prefers to occupy the tetrahedral interstitial site (t-site) in Ti–vanadium binary alloy. For the migration of He towards the vicinity of Ti, there is a significant repulsive interaction between Ti and neighboring tetrahedral He. Away from the Ti, He migrates from one t-site to another with a diffusion energy barrier of 0.06 eV, equal to that of He in pure vanadium. When He moves close towards the vicinity of Ti, its diffusion energy barrier can increase to ~0.19 eV at the first nearest neighbor t-site of the Ti. Thus, the presence of Ti can results in the increase of migration energy barrier of He. Concerning the formation of He_n cluster, we find that the binding energies the He_n cluster are energetically favorable due to the large binding energies among them. Such self-trapping of He atoms in Ti–vanadium alloy should be originated from the fast and easy diffusion property of interstitial He.

(ii) As to the effect of Ti on He_n-vacancy clusters, we find that with the presence of Ti in the vacancy vicinity, all the binding energies of He to He_{n-1}-vacancy cluster are found to decrease compared with that in pure vanadium. This demonstrates that the alloying element Ti can diminish the binding of He with vacancy in vanadium. Our results fully confirm that the retention and bubble of He in vanadium can be suppressed by doping the alloying element Ti in experiments. We also investigate the stability of small He_n-$vacancy_m$ (n/m = 1, 2, 3, 4) clusters in the dilute Ti–vanadium alloy. All the interactions between a tetrahedral He and the He_{n-1}-$vacancy_m$ cluster are attractive in the vicinity of Ti in vanadium. For a given value of m/n, the interstitial He binding energies to the cluster decreases/increases with the increasing number of He/vacancies. This fully demonstrates that the increase of cluster pressure stems from the gathering of He atoms.

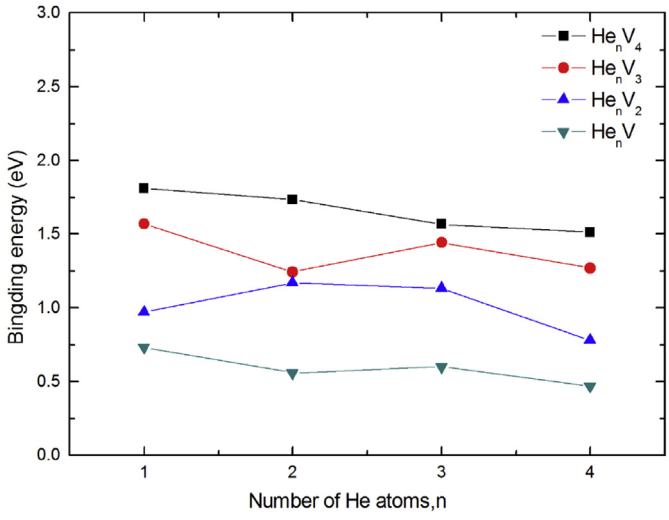

Fig. 7. The binding energies of the tetrahedral He to the He_{n-1}-$vacancy_m$ clusters.

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